SYNTHESIS AND REACTIONS OF ALIPHATIC SULFINIC ACIDS

BY

RAYNER SELBY JOHNSON

A. B., University of Mississippi, 1941

M. S., University of Nebraska, 1943

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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R. UNIV. BIBLIOTHEEK LEIDEN

SYNTHESIS AND REACTIONS OF ALIPHATIC SULFINIC ACIDS

Introduction

Mersolat, an emulsifier used successfully by German workers in their redox polymerizations, has been reported[1] to contain small amounts of aliphatic sulfinic acid salts. The German investigators thought that a considerable proportion of the activation obtained with this emulsifier was due to these sulfinates. In order to investigate the action of known quantities of sulfinate, which could be added to the various redox formulas, it was necessary to synthesize a number of aliphatic sulfinic acids. In the course of preparation of these acids, they were found to possess several unusual properties. Although a large amount of work has been reported on aromatic sulfinic acids, very little is known concerning the aliphatic series. The relatively few references to aliphatic sulfinic acids are mainly concerned with their synthesis, and very little has been reported in connection with their reactions. It thus became of interest to study some of the chemical properties of these acids.

Discussion of Results

Several methods of synthesis of aliphatic sulfinic acids have been investigated. Magnesium 1-dodecanesulfinate and magnesium 1-decanesulfinate were prepared by a modification of the methods of Houlton and Tarter[2] and Allen[3]. The Grignard reagents were prepared, treated with sulfur dioxide at −40°, and then hydrolyzed to give the magnesium salts. The sodium sulfinates were obtained by treatment of the magnesium salts with alcoholic sodium hydroxide. 1-Dodecanesulfinic acid was obtained by shaking the pure magnesium sulfinate with a mixture of ether and dilute hydrochloric acid. Treatment of an alkylmagnesium bromide with excess sulfur dioxide was found to give the alkyl alkanethiolsulfonate

as a result of disproportionation of the sulfinic acid which was found to be formed initially. Tetracosane and another substance having the composition of 1-dodecyl-1-dodecanethiolsulfinate were isolated as by-products of the reaction. The thiolsulfonate was readily hydrolyzed by alcoholic sodium hydroxide to the sodium sulfinate. *n*-Amylmagnesium bromide was allowed to react with *n*-heptaldehyde to give 6-dodecanol which was converted to 6-bromododecane by the action of anhydrous hydrogen bromide. Attempts to synthesize 6-dodecanesulfinic acid from the bromocompound by the Grignard method were not successful.

The synthesis of aliphatic sulfinic acids from ethylene disulfones was investigated. 1,2-Bis(1-dodecylthio)ethane was prepared by a modification of the method of Ziegler and Connor[4]. Ethylene bromide was caused to react with a slight excess of sodium 1-dodecyl mercaptide and the resulting ethylene disulfide then oxidized to 1,2--bis(1-dodecylsulfonyl)ethane with potassium permanganate in acetic acid. The ethylene disulfone was readily hydrolyzed with alcoholic potassium cyanide by the method of Ziegler and Connor[4] to give potassium 1-dodecanesulfinate and succinonitrile. It was found that hydrolysis of the 1,2-bis(1-dodecylsulfonyl)-ethane with alcoholic sodium hydroxide gave the sodium sulfinate along with β-(1-dodecylsulfonyl)diethyl ether. 1,2-Bis(6-dodecylthio)ethane was synthesized by allowing ethylene bromide to react with sodium 6-dodecyl mercaptide. This compound was also prepared by another method. Ethylene bromide was treated with thiourea to give ethylene diisothiouronium bromide. This salt was treated with alcoholic sodium hydroxide and the disodium salt of ethanedithiol which resulted was then allowed to react directly with 6-bromododecane without isolation. However, a better yield of the ethylene disulfide was obtained when the pure disodium salt of ethane dithiol was allowed to react with the bromocompound. The 1,2-bis(6-dodecylthio)ethane was then oxidized with potassium permanganate in acetic acid to give 1,2-bis(6-dodecylsulfonyl)ethane. Hydrolysis of this com-

pound with alcoholic potassium cyanide gave an amorphous solid which could not be crystallized. This solid showed 35 per cent sulfinate by nitrite titrations.

The synthesis of aliphatic sulfinic acids by reduction of the sulfonyl chlorides with zinc dust was also investigated. π-Hexadecanesulfonyl chloride (MPD-996 sulfonyl chloride) was reduced with zinc in both aqueous and alcoholic medium to give the zinc sulfinate which was then converted to the sodium sulfinate by the action of sodium carbonate.

6-Dodecanesulfinate was also prepared by a method similar to that of Claesson[5] A benzene solution of 6-dodecyl mercaptan was treated with sodium hydride and the resulting sodium mercaptide oxidized by the action of dry oxygen to sodium 6-dodecanesulfinate.

In seeking methods of identifying and determining aliphatic sulfinic acids in the presence of aliphatic sulfonic acids, the reactions of sodium alkanesulfinates with mercuric chloride and halogen alkylating agents were investigated. It was found that alkanesulfinates react in a manner analogous to that of the aromatic sulfinates. 1-Dodecylmercury chloride and 1-decylmercury chloride were prepared by treating the respective sodium sulfinates with mercuric chloride in boiling aqueous solution. Sodium 1-dodecanesulfinate was allowed to react with ethylene bromide to give 1,2-bis(1-dodecylsulfonyl)ethane and with monochloroacetic acid to give 1-dodecylsulfonylacetic acid. These derivatives were solids which gave sharp melting points.

The reaction of sulfinic acids with mercaptans reported by Von Braun and Weissbach[6] was further investigated. It was found by quantitative methods that the reaction was not a simple reduction by the mercaptan which was oxidized in the process to the disulfide as reported by them, but involved a common intermediate arising from the sulfinic acid and mercaptan which was thought to be the hypothetical sulfenic acid. For example, when 1-dodecanesulfinic acid

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and 1-dodecyl mercaptan were allowed to react, the yield of 1-dodecyl 1-dodecanethiolsulfonate was found to be more than twice the theoretical amount expected by the mechanism which was proposed by them. Several check runs were made which confirmed these results.

The reaction of aromatic sulfinic acids with nitrous acid is well known[7] although the analogous reaction of aliphatic sulfinic acids has apparently not been reported. Nitrous acid was found to react with 1-dodecanesulfinic acid in acetic acid solution to give N,N-di(1-dodecylsulfonyl)hydroxylamine. This compound was readily oxidized by excess nitrous acid to tri-(1-dodecylsulfonyl)amine oxide. Even with an equivalent amount of nitrous acid a small amount of the amine oxide was formed which explains why analysis by nitrite titrations are low. N,N-Di(1-dodecylsulfonyl)hydroxylamine was also readily oxidized by concentrated nitric acid in glacial acetic acid to the tri-(1-dodecylsulfonyl)amine oxide.

The decomposition of 1-dodecanesulfinic acid and salts was studied. When a pure sample of 1-dodecanesulfinic acid was sealed in a tightly stoppered bottle and allowed to stand for two months, 1-dodecyl 1-dodecanethiolsulfonate was isolated in good yield. I-Dodecanesulfinic acid was heated on a steam cone for two hours in a nitrogen atmosphere by the method of Von Braun and Weissbach[6] to give 1-dodecyl 1-dodecanethiolsulfonate and 1-dodecanesulfonic acid. A highly purified sample of magnesium 1-dodecanesulfinate was found to be 31 per cent oxidized to the magnesium sulfonate after standing in the air in powder form for four months. When a crude sample of magnesium 1-dodecanesulfinate was exposed to the air for six months it was found to be almost completely oxidized to the magnesium sulfonate.

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VITA

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